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Preparation of 2-Trialkylsiloxy-Substituted 1,3-Dienes and Their Diels–Alder/Cross-Coupling Reactions

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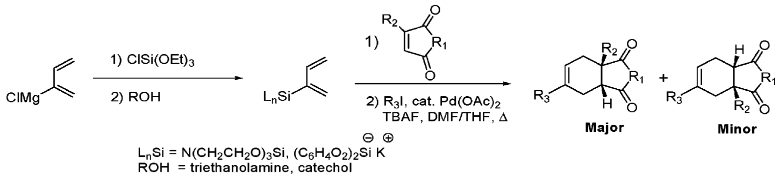
ABSTRACT



2-Triethylsiloxy-substituted 1,3-butadiene has been prepared in gram quantities from chloroprene via a simple synthetic procedure. Silatrane and catechol-substituted analogues of this main group element substituted diene were prepared by ligand exchange and characterized by X-ray crystallography in addition to standard spectroscopic techniques. Diels–Alder reactions of these dienes are reported as well as subsequent TBAF assisted/Pd-catalyzed Hiyama cross-coupling reactions of those Diels–Alder adducts.

Reports of main group element substituted 1,3-dienes and their reaction chemistry are not widespread in organic chemistry. With respect to silyl-substituted 1,3-dienes, 1-trimethylsilyl-1,3-butadiene was originally reported and trapped with maleic anhydride in 1957.[1] Fleming and co-workers then reported an alternate preparation of this compound and a number of its Diels−Alder reactions over the 1970s and early 1980s.[2,3] Subsequent to these initial reports a number of 1-silyl-1,3-diene preparations that rely on olefination of α,*β*-unsaturated aldehydes, nickel-catalyzed coupling reactions, etc. have also been reported and reviewed.[4,5] Reports of 2-silyl-substituted 1,3-dienes are 3- to 4-fold less frequent than their 1-substituted counterparts. 2-Triethylsilyl-1,3-butadiene and a few of its Diels−Alder reactions were reported by Ganem and Batt in 1978.[6] Paquette and Daniels reported some 2-silyl-substituted-1,3-cyclohexadienes in 1982 but none of their Diels−Alder chemistry.[7] Trost and Mignani reported the Pd-catalyzed elimination and cyclization reactions of 3-acetoxy-2-trimethylsilyl-1-butene in 1986.[8] Two other reports of the preparation of 2-trialkylsilyl-1,3-dienes have appeared since a 1995 review but neither of these studies report Diels−Alder reactions.[9,10] Reports of the preparation and use of 2-trialkoxysilyl-1,3-dienes are extremely rare. We find a report of the use of the Ganem and Batt protocol to make 2-trimethoxysilyl- and 2-triethoxysilyl-1,3-butadiene in 1984[11] and then a report of the polymerization of these materials in 1989.[12] Given the known propensity of trialkoxysilyl aryls and alkenyls to participate

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(1) Sadykh-Zade, S. I.; Petrov, A. D. *Dokl. Akad. Nauk SSSR* **1957**, *112*, 662.

(2) Fleming, I.; Percival, A. *J. Chem. Soc., Chem. Commun.* **1976**, 681−681.

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(4) Luh, T. Y.; Wong, K. T. *Synthesis* **1993**, 349−370.

(5) Stadnichuk, M. D.; Voropaeva, T. I. *Russ. Chem. Rev.* **1995**, *64*, 25−46.

(6) Batt, D. G.; Ganem, B. *Tetrahedron Lett.* **1978**, 3323−3324.

(7) Daniels, R. G.; Paquette, L. A. *Organometallics* **1982**, *1*, 1449−1453.

(8) Trost, B. M.; Mignani, S. *J. Org. Chem.* **1986**, *51*, 3435−3439.

(9) Kahle, K.; Murphy, P. J.; Scott, J.; Tamagni, R. *J. Chem. Soc., Perkin Trans. 1* **1997**, *7*, 997−999.

(10) Ikeda, Z.; Oshima, K.; Matsubara, S. *Org. Lett.* **2005**, *7*, 4859−4861.

(11) Sato, F.; Uchiyama, H.; Samaddar, A. K. *Chem. Ind.* (*London*) **1984**, 743−744.

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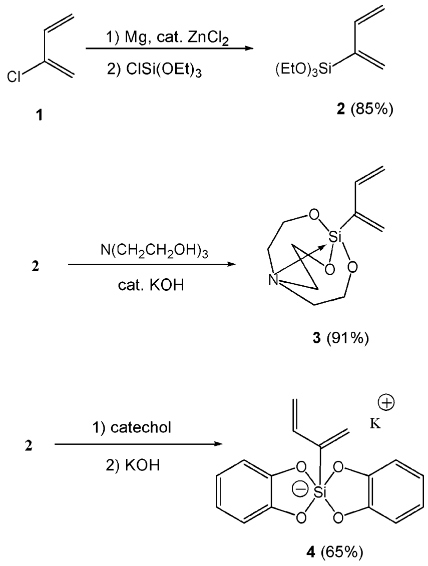
in fluoride-assisted, metal-catalyzed cross-coupling reactions,[13] we felt that an easily accessible preparation of 2-trialkoxysilyl-1,3-dienes would be subsequently useful for tandem Diels−Alder/cross-coupling chemistry. We report our initial studies in this area in the work that follows.

2-Trialkoxysilyl-Substituted 1,3-Diene Preparation and Characterization. 2-Triethoxysilyl-1,3-butadiene (**2**) was prepared in high yield by the nucleophilic addition of 1,3-butadienyl-2-magnesium chloride (generated in situ from chloroprene (**1**) and Mg) to triethoxysilyl chloride.[12,14] The title compound (**2**) was isolated as a colorless liquid after distillation under reduced pressure. This compound slowly polymerized on standing at room temperature over a period of 10−15 days but is quite stable at low temperature, −20 °C. 2-Triethoxysilyl-1,3-butadiene (**2**) can be used in ligand exchange reactions to make other siloxy dienes (**3**, **4**) as air stable crystalline solids. Alcoholysis of compound **2** with triethanolamine in the presence of a catalytic amount of KOH resulted in the formation of (buta-1,3-dien-2-yl)silatrane (**3**) as a light yellow solid. Treatment of **2** with catechol in the presence of KOH yielded potassium [bis(1,2-benzenediolato)-1,3-butadien-2-yl]silicate (**4**) as a white amorphous powder. At room temperature, compounds **3** and **4** show no signs of decomposition over a period of a few weeks.



All the silyl butadienes (**2**, **3**, and **4**) were structurally characterized by 1D and 2D NMR techniques. On the basis of the absence of NOESY cross-peaks between H1 ↔ H4 and H3 ↔ H1 and no observable peak broadening at temperatures down to −60 °C, we concluded that the *s-cis* to *s-trans* interconversion is too fast to observe in solution. Dienes **3** and **4** were both also characterized by single-crystal X-ray diffraction. Diene **3** proved to be unusual in that there were three independent molecules per asymmetric unit. Two of the three molecules in this unit had *s-trans* like diene torsion angles (C(17)−C(18)−C(19)−C(20) was 178.5(3)° and C(27)−C(28)−C(29)−C(30) was 170.3(3)°) whereas the third molecule had an *s-cis* like diene torsion angle (C(37)−C(38)−C(39)−C(40)) of 36.3(4)° (Figure 1). Diene **4** crystallizes with potassium coordinated THF molecules (Figure 2). The Si−C13 bond length is 1.889(5) Å and the diene torsion angle is very close to the *s-trans* 176.7(8)° (Figure 2).

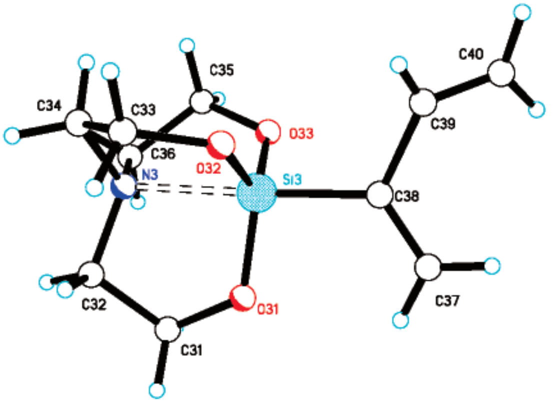


Figure 1. View of a molecule of the *s-cis* conformer of diene **3**.

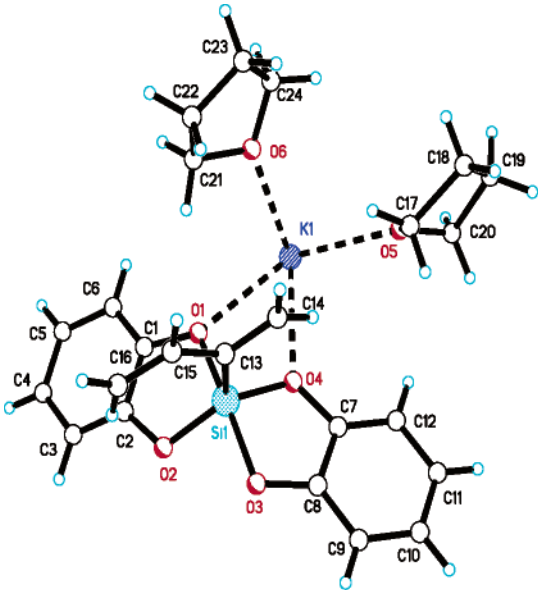


Figure 2. View of a molecule of diene **4** showing the coordinating THF solvent molecules.

Diels−Alder Reactions. We initially compared dienes **2**, **3**, and **4** in reactions with *N*-phenylmaleimide. We found that whereas the triethoxysilyl diene **2** showed only about a 2% conversion to cycloadduct **5** by NMR after 30 min at 25 °C in THF, the silatrane **3** and catechol containing dienes **4** showed complete conversion to cycloadducts **6** and **7** by ^{1}H NMR and the cycloadducts were subsequently isolated in almost quantitative yield.

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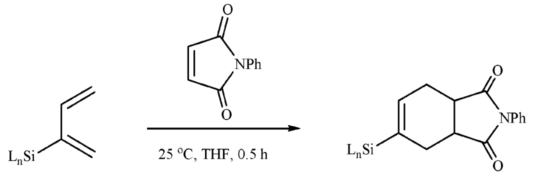
[13] Hiyama, T.; Shirakawa, E. *Top. Curr. Chem.* **2002**, *219*, 61−85.

[14] Nunomoto, S.; Yamashita, Y. *J. Org. Chem.* **1979**, *44*, 4788−4791.

Scheme 1. Reactions of 2-Trialkoxysilyl-1,3-dienes

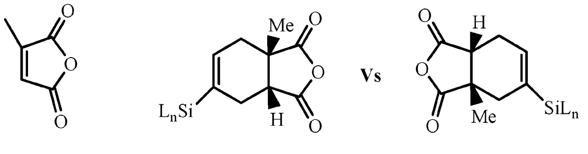


L_nSi = $(EtO)_3Si$ (**2**) **5** (2%)
= $N(CH_2CH_2O)_3Si$ (**3**) **6** (98%)
= $(C_6H_4O_2)_2Si^-K^+$ (**4**) **7** (99%)

We next wanted to get an idea of relative reactivity of these most reactive silicon-substituted dienes **3** or **4** in comparison to known, reactive dienes such as Danishefsky's diene (1-methoxy-3-trimethylsiloxy-1,3-butadiene).[15] We found that silatrane diene **3** reacted with *N*-phenylmaleimide at 0 °C with a k_{obs} of 3.7×10^{-2} min^{-1} and $t_{1/2}$ of 18.8 min whereas Danishefsky's diene reacted under identical conditions with a k_{obs} of 2.1×10^{-2} min^{-1} and a $t_{1/2}$ of 33 min. These data place the silatrane diene **3** at almost twice as reactive as Danishefsky's diene.

Single-point-energy, semiempirical (AM1) calculations of HOMO energies for a number of dienes, while constraining the 1,3-diene dihedral angles to 0°, were also performed with SPARTAN 2.0. 1,3-Butadiene, 2-methoxybutadiene, and Danishefsky's diene have HOMO energies of −9.35, −9.09, and −8.82 eV, respectively. Dienes **2**, **3**, and **4** have HOMO energies of −9.21, −7.87, and −5.04 eV, respectively. These energies are consistent with our observations that **2** is less reactive than Danishefsky's diene whereas **3** is more reactive than Danishefsky's diene and diene **3** is less reactive than diene **4**.

Additional Diels−Alder reactions with the unsymmetrical dienophile, citraconic anhydride **8**, were then performed to assess any differences in rate or regioselectivity of cycloaddition reactions. The silatrane-substituted diene **3** produced a 2.0:1 mixture of para:meta regioisomers (**9**:**10**) in 78% isolated yield after heating to 120 °C in THF for 48 h. The catechol silane-substituted diene (**4**) reacted under slightly milder conditions (90 °C for 36 h) to produce a 4.8:1 mixture of **11**:**12** in 78% isolated yield.



8 **Major** **Minor**

L_nSi = $N(CH_2CH_2O)_3Si$ **9** **10** (120 °C, 48 h, 78%, 2.0:1)
= $(C_6H_4O_2)_2Si^-K^+$ **11** **12** (90 °C, 36 h, 78%, 4.8:1)

Major and minor isomer regiochemistry and stereochemistry assignments were originally performed with NOESY data which showed strong NOEs between the CH_3 and both the ring junction H and one of the two diastereotopic H's on the CH_2 α to the alkene C−H for both **9** and **11**. This assignment was subsequently confirmed for the major isomer (**9**) by X-ray crystallography (Figure 3).

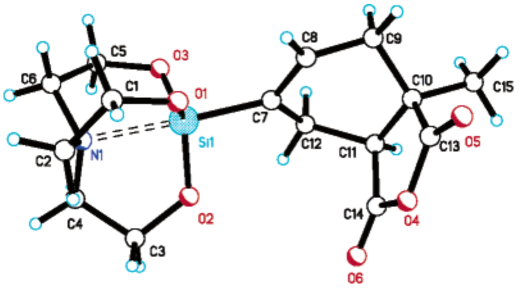
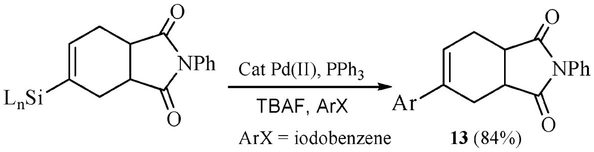


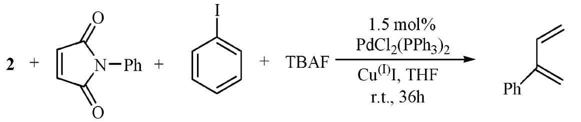
Figure 3. View of a molecule of major cycloadduct isomer **9**.

Diels−Alder/Cross Coupling. We have demonstrated that it is possible to effect Hiyama cross-coupling reactions of these silicon-substituted Diels−Alder cycloadducts.[16] Silatrane-substituted cycloadduct **6** was treated with iodobenzene or *p*-iodoanisole in the presence of Pd(II), PPh_3, and TBAF to produce the cross-coupled cycloadducts **13** and **14** in 83% and 68% isolated yield.

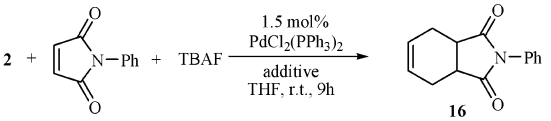


ArX = iodobenzene **13** (84%)
ArX = 4-iodoanisole **14** (68%)

We have also looked very briefly at the possibility of using these dienes in one-pot sequential reaction sequences rather than the two-pot Diels−Alder cross-coupling sequences described above. The first attempt to do transmetallation/Diels−Alder/cross coupling by treating **2** with *N*-phenylmaleimide, iodobenzene, and TBAF in the presence of Pd(II) and CuI just yielded the cross-coupling product of the silyl diene, 2-phenyl-1,3-butadiene (**15**).[17] The implication of this experiment is that transmetallation/oxidative addition/reductive elimination could not be intercepted by the Diels−Alder reaction under these conditions. A less ambitious transmetallation/Diels−Alder/protonolysis scheme did yield some Diels−Alder product **16**[18,19] from a one-pot reaction.



15 (72 %)



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additive	**% consumption of 2***	**% yield**
none	100	0*
$Cu^{(I)}I$	100	25
$ZnCl_2$	40	0*

* based on ^{1}HNMR

In summary, we have prepared new, stable, crystalline silyl-substituted dienes in high yield and find that they readily participate in Diels−Alder/cross-coupling tandem reactions. We will report the transition-metal-catalyzed reaction chemistry of these main group element substituted dienes in much more detail in due course.

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Supporting Information Available: Experimental procedures and characterization data for all new compounds and CIF files for compounds **3**, **4**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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